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# Improvement in tribological properties of chromium oxide coating at high temperature by solid lubricants

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## Abstract

The aim of the investigations was to improve the tribological properties of chromium oxide ( $\text{Cr}_2\text{O}_3$ ) coating for applications in heat engines at high temperatures. The experimental results show that the solid lubricants  $\text{CaF}_2$  and  $\text{BaF}_2$  in composite coatings can reduce and stabilize the friction coefficient, decrease the wear rate, prevent surface damage and improve the load capacity of  $\text{Cr}_2\text{O}_3$  coating at  $425^\circ\text{C}$  in air. In tribotests at 0.2–1.0 MPa it appears that the optimal solid lubricant content is around 14%–21% for  $\text{Cr}_2\text{O}_3$ – $\text{CaF}_2$  coatings and 20%–31% for  $\text{Cr}_2\text{O}_3$ – $\text{BaF}_2$  coatings. Auger electron spectroscopy and energy-dispersive spectroscopy analyses show that the friction coefficient is correlated with the amount of solid lubricant in contact areas: the friction coefficient decreases with solid lubricant content if it is less than 2%–4%, then stabilizes at about 0.20–0.25.

## 1. Introduction

Plasma-sprayed ceramic coatings such as zirconia and alumina have been applied to the combustion zone surfaces of different engines. They can ensure good thermal protection for components such as pistons, valves, upper liners, etc. The resulting improvements in engine durability and performance that have been experienced are significant and have led to increasing interest in the subject [1, 2]. However, the reduction in heat transfer resulting from the use of ceramic parts leads to a greater temperature rise in the cylinder walls of engines. These high temperatures, exceeding the cracking point of organic lubricants, generate dry sliding conditions between the liner and the piston ring [3]. In such cases the metallic parts cannot work because of their poor tribological properties under non-lubricated conditions at high temperatures. Consequently, an important task is to improve the tribological performance at high temperatures.

Ceramics, because of their good refractory properties, high hardness and good corrosion resistance, were considered as prospective candidate materials. Over a period of several years a large number of investigations have been carried out using different kinds of ceramics [4–8]. In comparison with metallic materials, ceramics have certainly improved the tribological performance, but the friction coefficient and wear rate of these materials are still too high for successful applications.

In order to improve the tribological properties of ceramics under severe sliding conditions, we have incorporated solid lubricants in the form of plasma-sprayed composite coatings [9]. The philosophy of these investigations is to exploit the high hardness of the ceramic matrix and the good properties of the solid lubricant.

The ceramic used in these studies is chromium oxide ( $\text{Cr}_2\text{O}_3$ ). It was selected according to the results of our experimental investigations [10, 11]. The solid lubricants used are calcium difluoride ( $\text{CaF}_2$ ) and barium difluoride ( $\text{BaF}_2$ ). They are considered as having good thermal and chemical stabilization and a strong lubrication effect [12].

## 2. Experimental details

### 2.1. Materials

The commercial  $\text{Cr}_2\text{O}_3$  powder used in these investigations has been produced by melting and crushing techniques. The experimental  $\text{CaF}_2$  and  $\text{BaF}_2$  powders have been developed by Rhône Poulenc; scanning electron microscopy (SEM) shows that both powders consist of angular and spongy particles. Table 1 presents some of their technical characteristics.

The composite coatings have been obtained by the atmospheric plasma spraying of powder mixtures on a mild carbon steel (35CD4) substrate that had been sand blasted with corundum. In order to improve the

TABLE 1. Technical characteristics of powders

Powder	Chemical composition (wt.%)	Powder description	Particle size ( $\mu\text{m}$ )
$\text{Cr}_2\text{O}_3$	94.97 $\text{Cr}_2\text{O}_3$ , 3 Fe, 1 Cr, 0.55 S, 0.45 Ca, 0.03 Mo		30-70
$\text{CaF}_2$	94 $\text{CaF}_2$ , 1.65 Si, 0.5 Mg, 0.09 Al, 0.03 Fe, 0.01 Mn, 0.01 Cu	Angular, spongy	70
$\text{BaF}_2$	96.91 $\text{BaF}_2$ , 0.33 Si, 0.01 Mg, 0.05 Al, 0.05 Fe, 0.93 Sr, 0.09 Ca, 0.335 O, 0.055 C	Angular, spongy	10

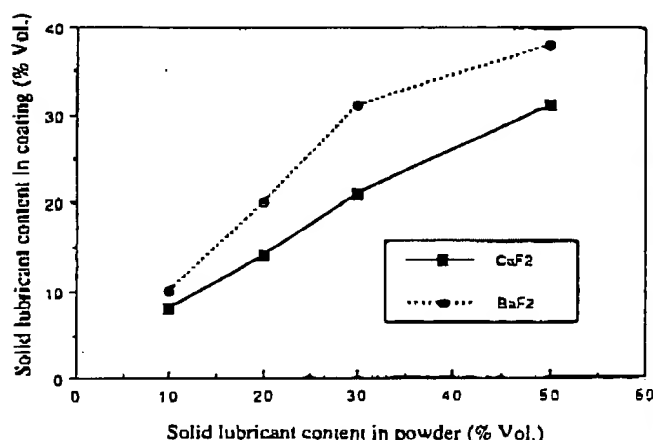
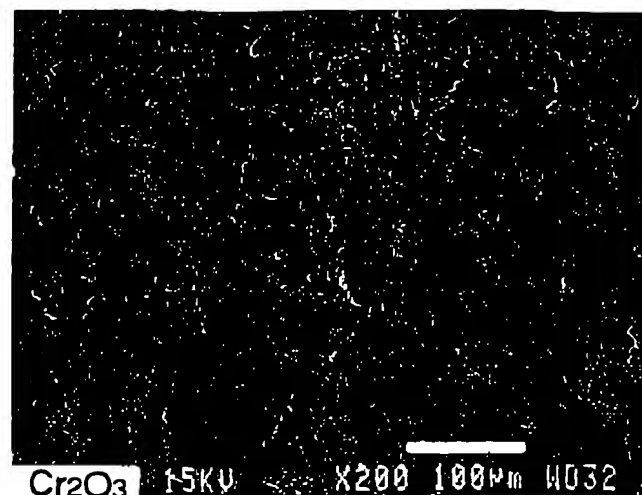


Fig. 1. Correlation between solid lubricant contents in powder mixtures and composite coatings.

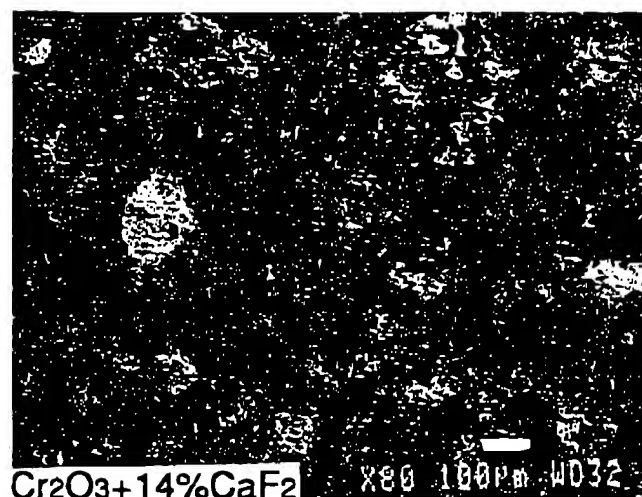
adherence of the coatings to the substrate, a bond coating of 80  $\mu\text{m}$  depth of pure  $\text{Cr}_2\text{O}_3$  was sprayed before deposition of the composite coating.

Chemical analysis shows that the solid lubricants are partially lost during spraying, especially for the  $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$  coatings, mainly because of the difference in their fusion points, which results in different evaporation rates. Figure 1 shows the correlation between the solid lubricant content of the powder mixture and that of the composite coating. Generally, this loss will increase with increasing solid lubricant percentage: the solid lubricant content in the coatings varies from 8% to 34%  $\text{CaF}_2$  for the  $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$  coatings and from 10% to 38%  $\text{BaF}_2$  for the  $\text{Cr}_2\text{O}_3$ - $\text{BaF}_2$  coatings when the solid lubricant content in the powder mixture varies from 10% to 50%.

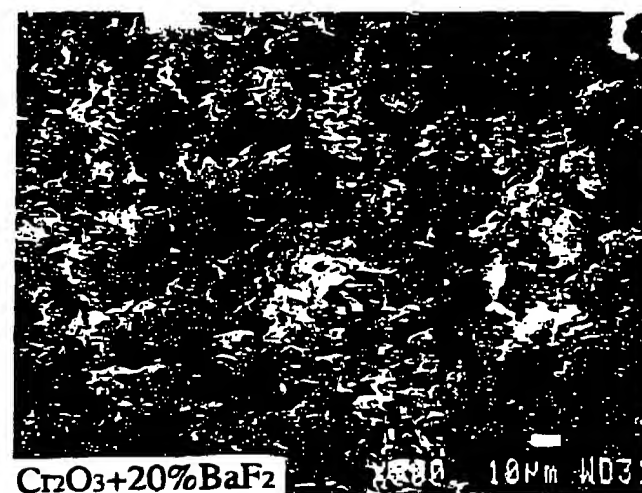
The coated surfaces have been observed by SEM. Some typical images are shown in Fig. 2. The composite coatings consist of a ceramic matrix ( $\text{Cr}_2\text{O}_3$ ) and solid lubricant particles dispersed in the matrix. The particle size is generally about 10  $\mu\text{m}$ , but some of them can be more than 100  $\mu\text{m}$ . Their shape is spheroidal. On the surface of the coatings we have observed some open pores. Statistical analysis of the  $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$  coatings shows that the porosity increases with increasing



(a)



(b)



(c)

Fig. 2. Initial microstructures of coatings: (a)  $\text{Cr}_2\text{O}_3$ , (b)  $\text{Cr}_2\text{O}_3$ -14% $\text{CaF}_2$ , (c)  $\text{Cr}_2\text{O}_3$ -20% $\text{BaF}_2$ .

solid lubricant content. Consequently, the coating density decreases and the roughness of the ground surface of the composite coating increases with increasing solid lubricant content.

Before sliding, we measured the Vickers hardness of the polished cross-section and of sliding surfaces with different roughnesses; *i.e.* ground and polished sliding surfaces. Figure 3 presents the hardness results. Although there is some scatter among these measurements due to differences in the roughness and structure as well as in the nature of the solid lubricants, we have found that the hardness decreases with increasing solid lubricant content and that the hardness of the  $\text{Cr}_2\text{O}_3$ - $\text{BaF}_2$  coatings is slightly lower than that of the  $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$  coatings.

In order to minimize the influence of the surface roughness on the friction and wear of the coatings, the sliding surface was lightly polished with abrasive paper of mesh 1000# to obtain samples with the same  $R_a$  ( $0.4 \mu\text{m}$  for the  $\text{Cr}_2\text{O}_3$  coating and  $0.6 \mu\text{m}$  for the  $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$  and  $\text{Cr}_2\text{O}_3$ - $\text{BaF}_2$  coatings). Before each test the samples were rinsed with denatured ethyl alcohol.

## 2.2. Apparatus and experimental conditions

All experiments were carried out using a tribometer specially designed for investigations of friction and wear in air at high temperatures [13, 14]. Its schematic description is given in Fig. 4. Rotation is provided by a spindle linked to an electric motor. Sliding occurs between two plasma-coated cylindrical ring surfaces of area  $286 \text{ mm}^2$  which are mounted on a stationary and a rotary spindle respectively. Normal load is applied through the stationary spindle by dead-weights hung on the loading arm when the normal load required is small (less than  $0.55 \text{ kN}$ ) and by a pneumatic system when the normal load is larger ( $0.55$ – $6.5 \text{ kN}$ ). The samples are heated to the required temperature, as measured by the thermocouples, using an electric furnace. The stationary spindle is restricted by a torque-sensing system which measures the friction coefficient at high temperatures ( $20$ – $1100^\circ\text{C}$ ). The friction force is recorded continuously.

All tests were carried out under the following conditions: environment, atmospheric air; temperature,  $425^\circ\text{C}$ ; sliding velocity,  $0.1 \text{ m s}^{-1}$ ; contact pressure,  $0.1$ – $22.1 \text{ MPa}$ , corresponding to a normal load of  $28.6$ – $6.32 \text{ kN}$ .

The total sliding time for most experiments was  $6 \text{ h}$ . Damage processes were followed by optical microscopy and SEM, interrupting the motion after  $0.5$ ,  $2$  and  $4 \text{ h}$  of sliding. Wear was characterized from the mass loss of both discs after taking into consideration the oxidation weight gain of the metallic substrate (see Appendix).

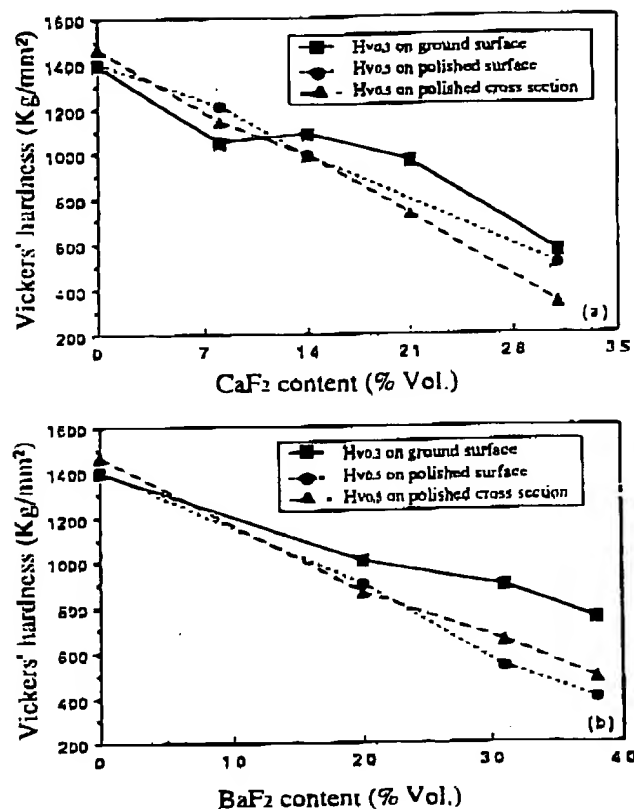


Fig. 3. Evolution of Vickers hardness of (a)  $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$  and (b)  $\text{Cr}_2\text{O}_3$ - $\text{BaF}_2$  with solid lubricant content.

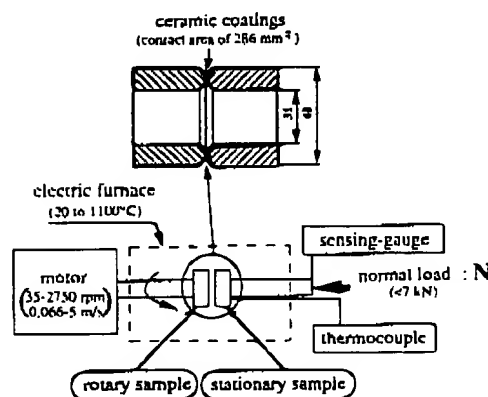


Fig. 4. Schematic operating principle of the tribometer.

## 3. Experimental results

Five friction couples –  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$ ,  $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2/\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$ ,  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$ - $\text{BaF}_2$  and  $\text{Cr}_2\text{O}_3$ - $\text{BaF}_2/\text{Cr}_2\text{O}_3$ - $\text{BaF}_2$  – have been tested. The results will be presented in terms of the following three aspects:

- (1) improvement in tribological properties of  $\text{Cr}_2\text{O}_3$  coating by solid lubricant addition;
- (2) influence of solid lubricant content, nature and distribution on friction coefficient and wear rate;

(3) tribological properties of the coatings under high pressure.

### 3.1. Improvement in tribological properties of $\text{Cr}_2\text{O}_3$ coating

Comparing the friction and wear of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$  with those of the other couples, we find that the solid lubricants improve the tribological properties of the  $\text{Cr}_2\text{O}_3$  coating. Figure 5 shows typical friction curves of tribotests carried out under the same conditions. Two observations can be derived from them. Firstly, for the friction of pure  $\text{Cr}_2\text{O}_3$ , the stick-slip phenomenon occurs and a considerable variation in the friction coefficient is observed. When a solid lubricant is introduced in one or both coatings, the variation in the friction coefficient becomes much smaller and the stick-slip phenomenon disappears. Secondly, the mean friction coefficient without solid lubricant is about 0.4, but it is much smaller and varies between 0.2 and 0.25 if there is a solid lubricant in the coating(s).

Figure 6 presents the evolution of mass loss vs. sliding distance under a pressure of 0.2 MPa. It shows that this evolution can be distinguished by two different stages:

(1) At the beginning of a test the mass loss is significant. Microscopic observations show that this results from surface polishing, which produces considerable wear because of the removal of some sharp asperities. For the test under pressures between 0.2 and 1.0 MPa this stage is shorter than 30 min.

(2) After the running-in stage the wear of the coating becomes more stable and regular and the mass loss increases linearly. To evaluate the wear resistance of different coatings, we have used the "wear rate  $K_v$ " term, which is defined by the formula

$$K_v = \frac{\Delta m}{\rho P S V t}$$

where  $\Delta m$  is the mass loss of the two samples of one couple,  $\rho$  is the mean density of the coatings,  $P$  is the apparent pressure,  $S$  is the nominal contact area,  $V$  is the sliding velocity and  $t$  is the sliding time.

Table 2 presents wear rates and mean friction coefficients of different couples under pressures of 0.2, 0.5 and 1.0 MPa. It is seen that the solid lubricants can reduce the wear rate considerably.

Figure 7 presents photographs of the surfaces of  $\text{Cr}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ -14% $\text{CaF}_2$  and  $\text{Cr}_2\text{O}_3$ -20% $\text{BaF}_2$  after 6 h of sliding under a pressure of 0.2 MPa against  $\text{Cr}_2\text{O}_3$ . They show that the  $\text{Cr}_2\text{O}_3$  surface after sliding against  $\text{Cr}_2\text{O}_3$  has been damaged and is characterized by the removal of material in some contact areas with strong adhesion. However, when a solid lubricant is introduced in the coating(s), the surfaces of the samples made of  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ -solid lubricant become macroscopi-

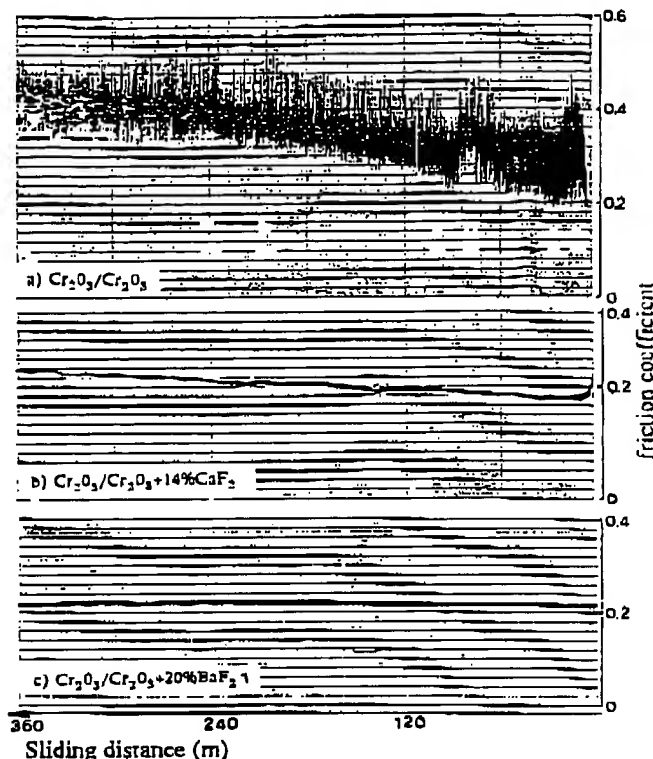


Fig. 5. Friction curves under 0.2 MPa.

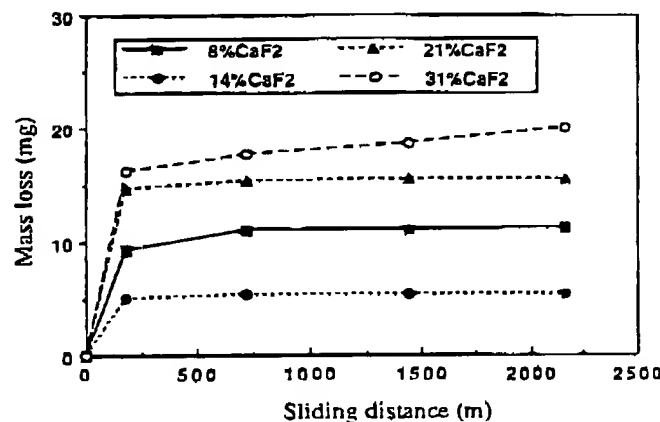


Fig. 6. Variation in mass loss with sliding distance for  $\text{Cr}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$  under 0.2 MPa.

cally very smooth, while microscopically they are characteristic of the formation of contact plateaux via plastic deformation; we have not observed any extensive surface damage.

### 3.2. Influence of solid lubricant content, nature and distribution

#### 3.2.1. Influence of solid lubricant content

The solid lubricant content exerts an important influence on the tribological properties. Figure 8 presents the variations in friction coefficient and wear rate

TABLE 2. Mean friction coefficient  $f$ , friction coefficient dispersion amplitude  $\Delta f$  and wear rate  $K$ , under 0.2, 0.5 and 1.0 MPa

Friction materials*	Contact pressure (MPa)								
	0.2			0.5			1.0		
	$f$	$\Delta f$	$K$ ( $10^{-6} \text{ mm}^3$ $\text{N}^{-1} \text{ m}^{-1}$ )	$f$	$\Delta f$	$K$ ( $10^{-6} \text{ mm}^3$ $\text{N}^{-1} \text{ m}^{-1}$ )	$f$	$\Delta f$	$K$ ( $10^{-6} \text{ mm}^3$ $\text{N}^{-1} \text{ m}^{-1}$ )
$\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$	0.42	0.1	6.5	0.35	0.04	6.1	0.32	0.02	5.0
$\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-x\%\text{SL}$									
SL: $\text{CaF}_2$ $x=8$	0.25	0.005	0.23	0.30	0.006	0.66	0.58	0.008	4.1
14	0.25	0.003	0.16	0.26	0.003	0.13	0.27	0.003	0.06
21	0.26	0.003	0.05	0.23	0.003	0.25	0.26	0.003	0.12
34	0.26	0.004	4.7	0.26	0.004	3.0	0.26	0.005	1.9
SL: $\text{BaF}_2$ $x=10$	0.29	0.004	0.51	0.25	0.004	0.12	0.27	0.005	0.06
20	0.24	0.003	0.88	0.24	0.003	0.13	0.25	0.003	0.02
31	0.25	0.003	0.09	0.22	0.003	0.06	0.23	0.003	0.12
$\text{Cr}_2\text{O}_3-x\%\text{SL}/\text{Cr}_2\text{O}_3-x\%\text{SL}$									
SL: $\text{CaF}_2$ $x=14$	0.27	0.004	0.08	0.27	0.004	0.07	0.28	0.004	0.3
21	0.27	0.004	0.13						
34	0.27	0.004	5.6	0.26	0.004	1.7	0.25	0.004	2.7
SL: $\text{BaF}_2$ $x=20$	0.27	0.003	0.09	0.27	0.003	0.09	0.27	0.003	0.03
31	0.26	0.003	0.08	0.25	0.003	0.07	0.27	0.003	0.06
38	0.26	0.003	0.85	0.24	0.003	0.12	0.23	0.003	0.62

\*SL, solid lubricant.

vs.  $\text{CaF}_2$  content for friction of the  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3\text{-CaF}_2$  couple, while Fig. 9 presents those for the  $\text{Cr}_2\text{O}_3\text{-BaF}_2/\text{Cr}_2\text{O}_3\text{-BaF}_2$  test. They show that a low solid lubricant content generally produces a high friction coefficient and a substantial wear rate. On increasing the solid lubricant content, the friction coefficient first decreases and then stabilizes at about 0.2–0.25. However, we have observed optimal content ranges for the wear rate: 14%–21%  $\text{CaF}_2$  for  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3\text{-CaF}_2$  sliding and 20%–31%  $\text{BaF}_2$  for  $\text{Cr}_2\text{O}_3\text{-BaF}_2/\text{Cr}_2\text{O}_3\text{-BaF}_2$  sliding. These phenomena can be explained by the different influences of the solid lubricant on the tribological and mechanical properties of the coatings: an increase in the solid lubricant percentage can certainly improve the tribological properties, but it also produces a degradation in the mechanical properties. This is the reason why coatings with a medium content of solid lubricant show the best performance.

### 3.2.2. Influence of solid lubricant nature

Figure 10 compares the friction coefficients and wear rates of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-x\%\text{CaF}_2$  sliding with those of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-x\%\text{BaF}_2$  ( $x$  is the solid lubricant content by volume in the powder mixtures). It shows that the sliding friction coefficient of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-x\%\text{BaF}_2$  is slightly lower than that of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-x\%\text{CaF}_2$ , while their wear rates show the same trend. This small difference between the two kinds of solid lubricant may

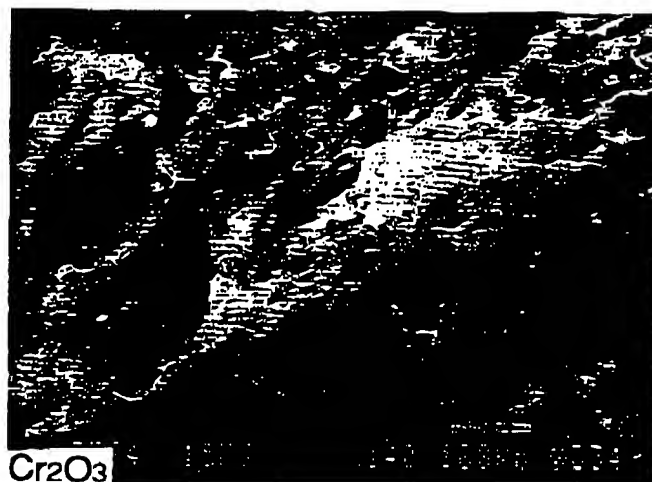
result from their different hardnesses, i.e. the hardness ratios of  $\text{Cr}_2\text{O}_3$  and the solid lubricants will be different, which will result in a slightly different friction coefficient [15].

### 3.2.3. Influence of solid lubricant distribution

Figure 11 compares the friction coefficients and wear rates of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-x\%\text{CaF}_2$  sliding with those of  $\text{Cr}_2\text{O}_3-x\%\text{CaF}_2/\text{Cr}_2\text{O}_3-x\%\text{CaF}_2$  ( $x$  is the solid lubricant content by volume in the coatings). Generally,  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-x\%\text{CaF}_2$  has a lower sliding friction coefficient than  $\text{Cr}_2\text{O}_3-x\%\text{CaF}_2/\text{Cr}_2\text{O}_3-x\%\text{CaF}_2$ , while their wear rates are of the same magnitude. Similar phenomena have been observed in sliding with  $\text{Cr}_2\text{O}_3-x\%\text{BaF}_2$  coatings. Figure 12 compares the friction coefficients and wear rates of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-x\%\text{BaF}_2$  sliding with those of  $\text{Cr}_2\text{O}_3-x\%\text{BaF}_2/\text{Cr}_2\text{O}_3-x\%\text{BaF}_2$  ( $x$  is the solid lubricant content by volume in the coatings).

### 3.3. Tribological properties of the coatings under high pressure

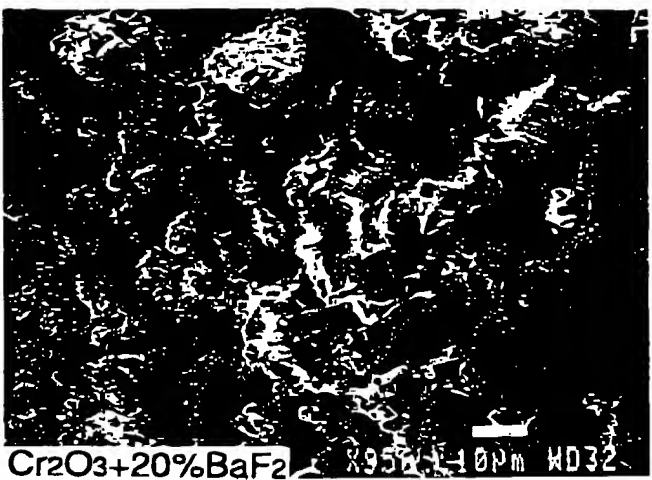
It is very important to determine the maximal pressure of the coatings for applications. For this purpose we have measured the friction coefficients and wear rates of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3\text{-14}\%\text{CaF}_2$  sliding under high pressures up to 22.1 MPa and generally confirmed the reduction in friction coefficient and wear rate by solid lubricant addition even under high pressure.



(a)



(b)



(c)

Fig. 7. Surface damage of (a)  $\text{Cr}_2\text{O}_3$ , (b)  $\text{Cr}_2\text{O}_3$ -14% $\text{CaF}_2$  and (c)  $\text{Cr}_2\text{O}_3$ -20% $\text{BaF}_2$  after 6 h of sliding against  $\text{Cr}_2\text{O}_3$  under 0.2 MPa.

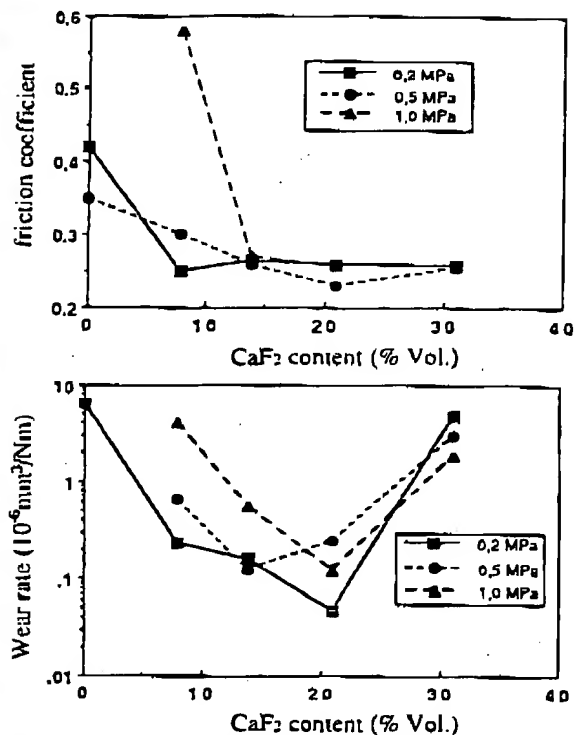


Fig. 8. Evolution of friction coefficient and wear rate of  $\text{Cr}_2\text{O}_3$ / $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$  with  $\text{CaF}_2$  percentage.

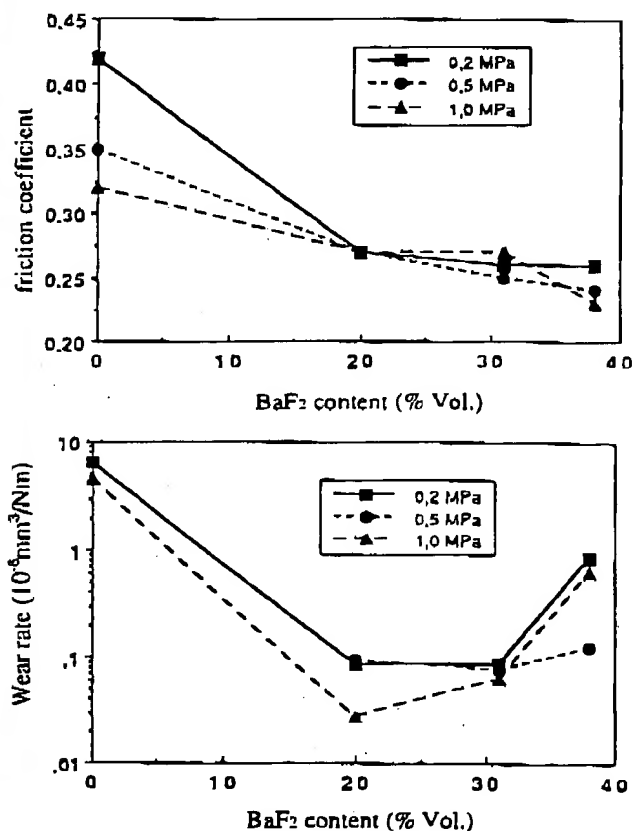


Fig. 9. Evolution of friction coefficient and wear rate of  $\text{Cr}_2\text{O}_3$ - $\text{BaF}_2$ / $\text{Cr}_2\text{O}_3$ - $\text{BaF}_2$  with  $\text{BaF}_2$  percentage.



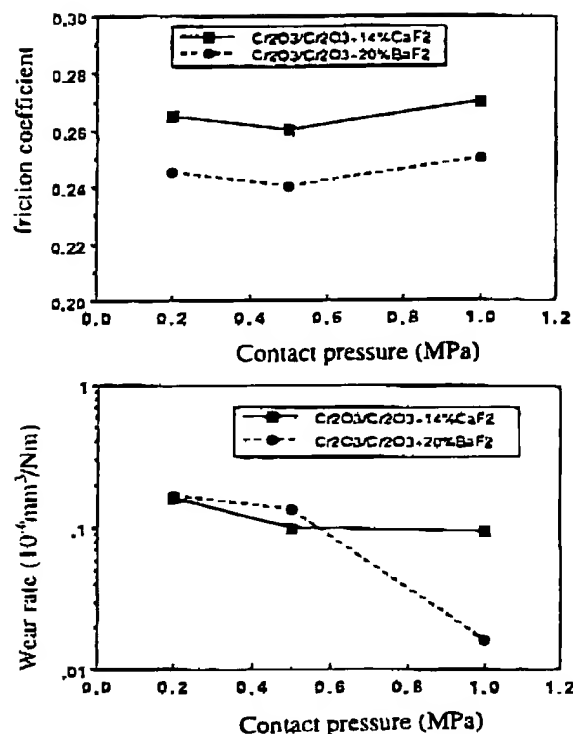


Fig. 10. Comparison of friction coefficient and wear rate of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-14\%\text{CaF}_2$  and  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-20\%\text{BaF}_2$  under 0.2 MPa.

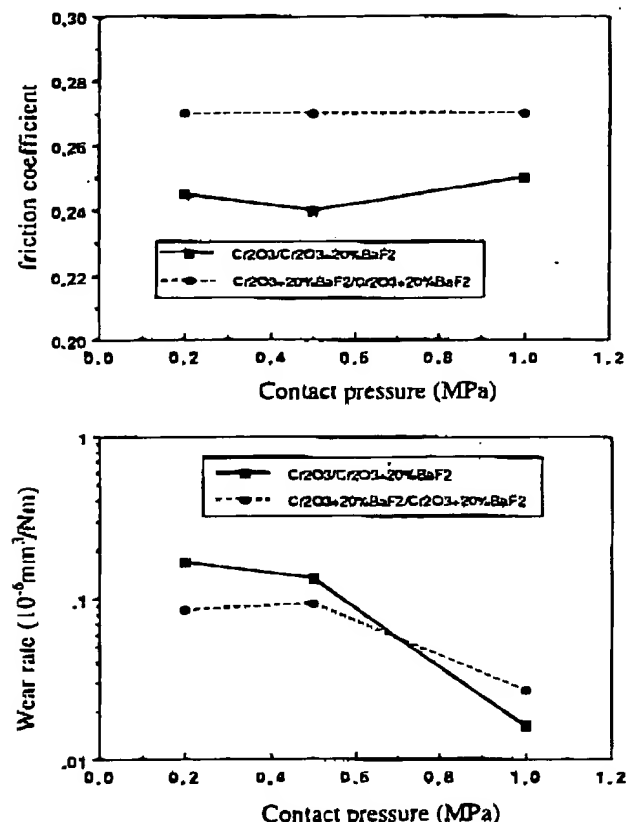


Fig. 12. Comparison of friction coefficient and wear rate of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-20\%\text{BaF}_2$  and  $\text{Cr}_2\text{O}_3-20\%\text{BaF}_2/\text{Cr}_2\text{O}_3-20\%\text{BaF}_2$ .

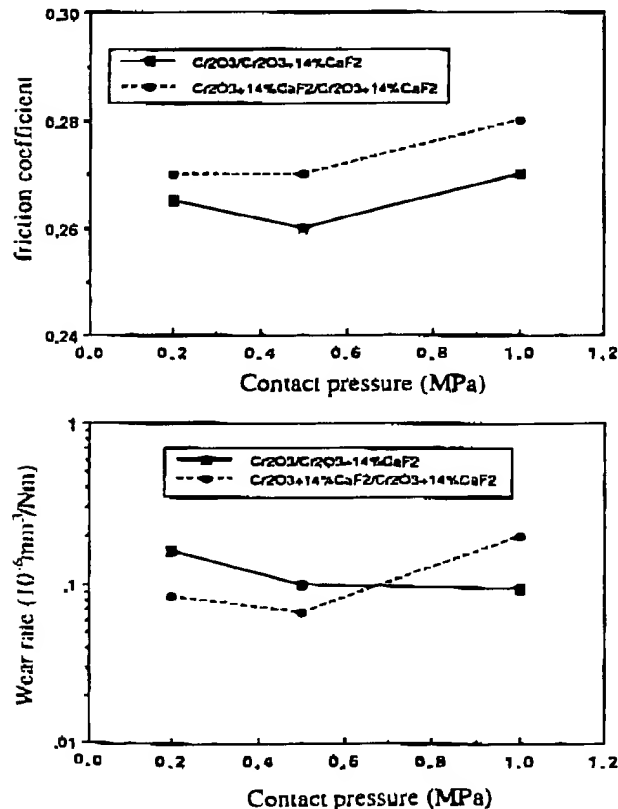


Fig. 11. Comparison of friction coefficient and wear rate of  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-14\%\text{CaF}_2$  and  $\text{Cr}_2\text{O}_3-14\%\text{CaF}_2/\text{Cr}_2\text{O}_3-14\%\text{CaF}_2$ .

It is important to point out that although  $\text{Cr}_2\text{O}_3$ -solid lubricant coatings are less hard than pure  $\text{Cr}_2\text{O}_3$  coating, the increase in critical load achieved by using a solid lubricant in the tribological case is clearly evident: for  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$  sliding, chevron-shaped cracks have been observed under a pressure of 14.5 MPa; however, for  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3-14\%\text{CaF}_2$  sliding, the cracking pressure increases from 14.5 (4.15) to 22.1 MPa (6.32 kN). This improvement in load capacity of the coating probably results from the reduction in friction coefficient brought about by the solid lubricant, i.e. the tangential load will decrease and consequently the critical load will obviously increase [16].

#### 4. Characterization of the sliding surfaces and discussion

By use of Auger electron spectroscopy (AES) we have analysed the contact areas (contact plateaux) and non-contact areas of  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3-14\%\text{CaF}_2$  coating surfaces after 6 h of sliding. Figure 13 presents the results of a typical analysis of the  $\text{Cr}_2\text{O}_3$  coating surface. We have found that the spectrum obtained in the contact area contains one calcium peak with a significant amplitude, whereas this peak does not exist in the non-

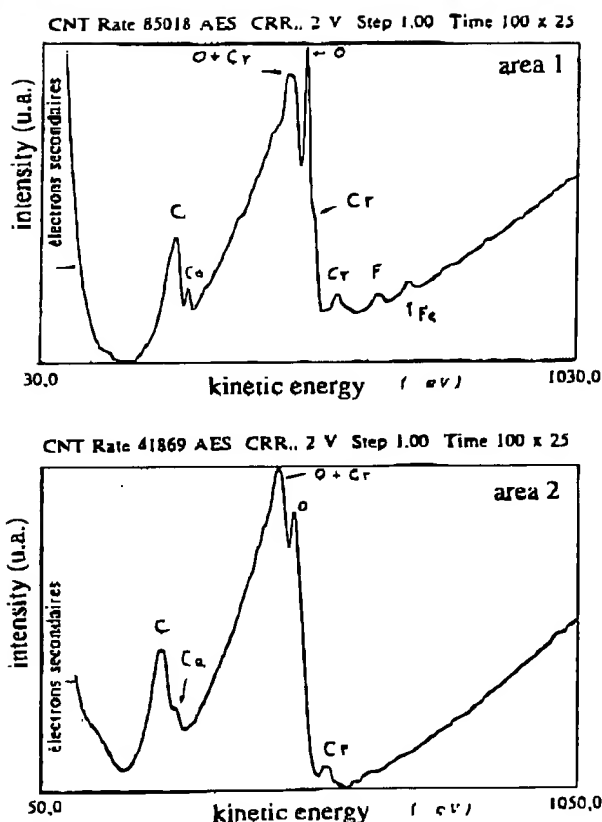
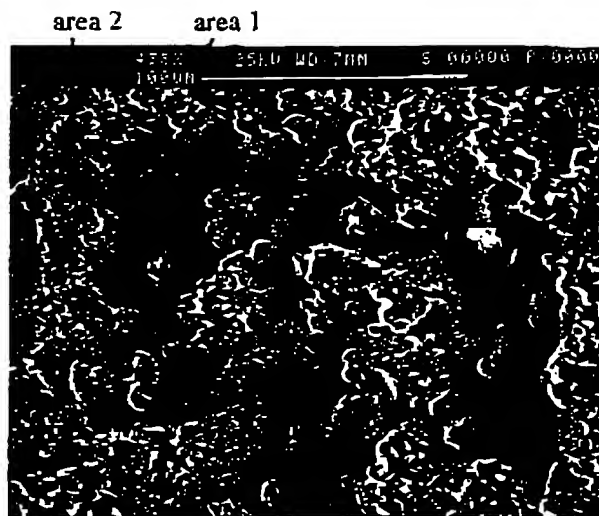


Fig. 13. Results of AES analysis of contact and non-contact areas on  $\text{Cr}_2\text{O}_3$  surface after 6 h of sliding against  $\text{Cr}_2\text{O}_3$ -14% $\text{CaF}_2$  under 0.2 MPa.

contact area. These analyses indicate that sliding can enrich the solid lubricant on the surface, thus inducing an improvement in friction and wear properties.

In order to confirm this idea, a large number of analyses by energy-dispersive spectroscopy (EDS) have been carried out on different worn specimens. Figure

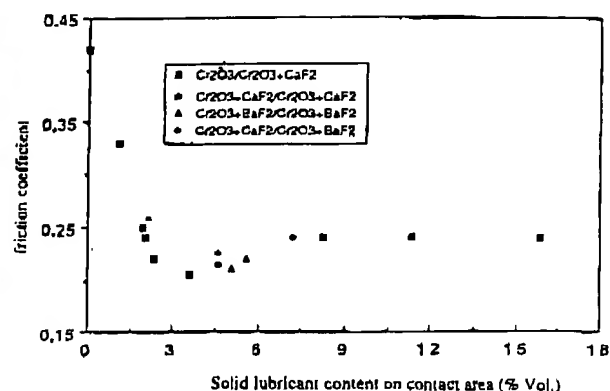


Fig. 14. Correlation between friction coefficient and solid lubricant (resulting from material transfer) content on contact area.

14 presents the relation between friction coefficient and mean solid lubricant content of three to five measurements on contact areas of various specimens. It shows that the friction coefficient first decreases with solid lubricant content if it is less than 2%–4% and then stabilizes at about 0.20–0.25 when the solid lubricant content is more than 4%. Thus the good friction and wear properties of the composite coatings probably result from the solid lubricants on contact areas producing two important effects:

- (1) a reduction in adhesion strength, which restricts the formation of adhesive junctions [11];
- (2) the presence of a soft superficial layer ( $\text{CaF}_2$  or  $\text{BaF}_2$ ) which reduces the proportion of shearing resistance at the yield point of the hard material ( $\text{Cr}_2\text{O}_3$ ) [15].

## 5. Conclusions

(1) The tribological performance of  $\text{Cr}_2\text{O}_3$  coating can be improved by the incorporation of solid lubricants ( $\text{CaF}_2$  and  $\text{BaF}_2$ ). The mean friction coefficient has been reduced from about 0.4 for  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$  sliding to 0.2–0.25 for  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$ -solid lubricant sliding; the friction curve of the  $\text{Cr}_2\text{O}_3$  coatings with solid lubricant becomes much more stable than that of pure  $\text{Cr}_2\text{O}_3$  coating.

(2) Solid lubricant addition has also improved the wear resistance of  $\text{Cr}_2\text{O}_3$  coating; the wear rate has been decreased from  $6.5 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  for  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$  sliding to about  $10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  for  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$ -solid lubricant sliding.

(3) The solid lubricant can improve the load capacity of  $\text{Cr}_2\text{O}_3$  coating. The cracking pressure increases from 14.5 MPa (4.15 kN) for  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$  to 22.1 MPa (6.32 kN) for  $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_3$ -14% $\text{CaF}_2$ .

(4) The optimal solid lubricant content is around 14%–21% for  $\text{Cr}_2\text{O}_3$ - $\text{CaF}_2$  coatings and 20%–31% for  $\text{Cr}_2\text{O}_3$ - $\text{BaF}_2$  coatings.

